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Self-propagating high-temperature synthesis of Ce-bearing zirconolite-rich minerals using $Ca(NO_3)_2$ as the oxidant

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HIGHLIGHTS

- Zirconolite was synthesized by SHS using $Ca(NO_3)_2$ as the oxidant.
- T_{ad} was calculated to evaluate the sustainability of SHS with $Ca(NO_3)_2$ oxidant.
- The selected sample was readily solidified with density of 4.62 g/cm^3.
- CeO_2 was successfully immobilized into the SHS-ed Synroc.

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ABSTRACT

Synroc is recognized as the second generation waste form for the immobilization of high-level radioactive waste (HLW). Zirconolite-rich ($CaZrTi_2O_7$) Synroc minerals were attempted by self-propagating high-temperature synthesis (SHS) using Fe_2O_3, CrO_3, $Ca(NO_3)_2$ as the oxidants and Ti as the reductant. All designed reactions were ignited and sustained using $Ca(NO_3)_2$ as the oxidant, and zirconolite-rich ceramic matrices were successfully prepared with pyrochlore ($Ca_2Ti_2O_6$), perovskite ($CaTiO_3$) and rutile (TiO_2) as the minor phases. The sample CN-4, which was designed using $Ca(NO_3)_2$ as the oxidant with TiO_2/Ti ratio of 7:9, was readily solidified with density of 4.62 g/cm^3 and Vickers hardness of 1052 HV. CeO_2 was successfully stabilized by the CN-4 sample with resultant phase constituent of 2M-$CaZrTi_2O_7$ and $CaTiO_3$.

1. Introduction

The disposal of high-level radioactive waste (HLW) from spent nuclear fuel reprocessing of commercial or military reactors has been a great challenge in nuclear industry [1]. Because of their high radiotoxicity and long half-life, minor actinides (MA), such as Np, Am and Cm, are the primary concern for HLW immobilization [2,3]. Highly stable and durable matrices, such as glasses, glass-ceramics and monophasic or assemblages of ceramics, have been explored for long-term disposal of HLW [4–7]. At present, vitrification by borosilicate and phosphate glasses is the exclusive approach for industrial scale operations of HLW management [1]. However, the low solubility of minor actinides in glass matrix and the metastable nature of glasses are the major limitations [8,9]. On the other hand, Synroc has been recognized as a promising host material for HLW immobilization [2–7,10], which is mainly composed of multiple mineral phases, such as zirconolite ($CaZrTi_2O_7$), pyrochlore ($A_2B_2O_6X$), perovskite ($CaTiO_3$), hollandite ($BaAl_2Ti_6O_{16}$), rutile (TiO_2), spinel (AB_2O_4) and nepheline ($KNa_3(AlSiO_4)_4$). Based on the isomorphism substitution, radioactive nuclides can be incorporated into the lattice structure of above-mentioned mineral phases, leading to promoted long-term stability and safety [11–13].

In the Synroc family, zirconolite is one of the most important constituent phases. Because of its crystal structure, zirconolite holds the capacity to accommodate various cations in a wide range of valence and ionic radii, such as rare-earths, actinide, alkaline earth

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ions and smaller cations like transition metal ions [2,3,11,14–21]. In addition, zirconolite structure-typed materials demonstrate high leach resistance, excellent thermal and radiation stabilities [22–27]. Thus, zirconolite was recognized as the main phase for safe immobilization of actinides, and substantial researches have been conducted in the past decades [28–35]. Zirconolite-rich Synroc waste forms were mainly synthesized from two routes [3–6]: (1) liquid phase synthesis (such as hydroxide and sol–gel methods) and (2) solid state reaction. Zirconolite was mostly prepared under high temperature (≥1200 °C) from these approaches. Meanwhile, compulsive densification processes with high pressure were usually required to obtain highly compacted samples [33]. The requirement of high temperature and pressure leads to high cost and complicated synthesis process for zirconolite-rich Synroc waste forms.

Muthuraman et al. [36,37] have proposed a novel synthesis approach, self-propagating high-temperature synthesis (SHS), for the management of nuclear wastes. SHS is an exothermic chemical reaction, which consumes a small amount of external energy and releases a large amount of heat [38–40]. Once ignited, the combustion of SHS reactions can be sustainably conducted. Compared with the conventional solid state reaction processes, SHS leads to high temperature and reaction speed, as well as low energy consumption, low cost, simplified equipment requirement and convenient handling. Ojovan and co-workers have analysed the self-sustaining immobilization of radioactive wastes in mineral-like and glass composite materials using SHS technique [41–44]. Zhang et al. [45] have investigated the SHS preparation of perovskite ($CaTiO_3$) using Fe_2O_3 and CrO_3 as the oxidants. Sr was readily immobilized into the Ca site of perovskite, which resulted in high inclusion content and promoted stability. Borovinskaya et al. [46–50] have employed the SHS technique to synthesize perovskite, zirconolite, rutile and pollucite mineral phases for HLW immobilization. Perovskite-based mineral waste forms were prepared using $Ca(NO_3)_2$ and Fe_2O_3 mixed oxidant [49]. However, zirconolite was not obtained as the main phase in previously designed SHS reactions. The obtained main phases were perovskite, rutile and pollucite. Recently, $Y_2Ti_2O_7$ pyrochlore-rich Synroc was successfully synthesized from SHS processing using MoO_3 as the oxidant and Ti as the reductant [51].

In this study, zirconolite-rich Synroc minerals were explored by SHS using Fe_2O_3, CrO_3, $Ca(NO_3)_2$ as the oxidants and Ti as the reductant. Although these oxidant systems were studied previously, the composition of raw reactants was not informed. Meanwhile, the effects of single oxidant (Fe_2O_3, CrO_3 and $Ca(NO_3)_2$) and reactant composition on resultant product were rarely reported. As the Ti source of zirconolite, the ratio of TiO_2 and Ti was tailored in the raw reactants to regulate the composition. The adiabatic temperatures (T_{ad}), which is an important parameter to predict sustainability of the SHS reactions [52], were calculated under different oxidants and TiO_2/Ti ratios. The effects of different oxidant and reactant composition on the SHS temperature and resultant product were explored systematically. As the simulant of tetravalent actinides [34], 10 at% CeO_2 was doped to replace the Zr site of zirconolite. Silimar as previous report [53], the immobilization behavior of Ce in zirconolite was explored as well in the SHS process.

2. Experimental details

Fe_2O_3, CrO_3, $Ca(NO_3)_2$, CaO, Ti, TiO_2 (Anatase), ZrO_2 and CeO_2 with purity higher than 99 wt% and particle size less than 200 mesh were purchased from Aladdin Industrial Inc as the raw materials. Fe_2O_3, CrO_3 and $Ca(NO_3)_2$ were employed as the oxidants with Ti as the reductant. The designed powder charge of about 20 g was dry ground mechanically for 30 min and pressed at 20 MPa using 25 mm Φ stainless mould. The SHS process was conducted as illustrated in Fig. 1. Silica sand with granularity of 40–70 mesh was employed as the heat insulator and pressure transmission medium. Firstly, the real temperatures during combustion were measured before the sample was compressed. The temperature tendency curves, which could be valuable as a guide for the compression process, were recorded by a XME2002/U paperless recorder connected with the W/Re 5/26 thermocouple.

After the temperature measurement, a new sample was employed for subsequent SHS and compression process. Bottom of the stainless steel mould was covered with silica sand. The preformed green bodies were embedded into the silica sand as illustrated in Fig. 1. The specimens were subsequently ignited by a tungsten wire, which was located at one side in tight contact with the specimens. The tungsten wire was motivated by a direct current of about 50 A. The green bodies of SHS reactants were ignited and combusted instantly under the heat radiation of tungsten wire.

The optimal sample was selected to explore the densification and simulated nuclide immobilization processes. After completion of 10 s combustion, this sample was compressed at 40 MPa by a hydraulic press machine with holding time of 60 s. The whole combustion and compression process takes no more than 3 min. As a simulant of tetravalent actinides, 10 at% CeO_2 was added to replace the Zr site of zirconolite. After cooling, the solidified specimens were cutted and polished to 2000 mesh for further characterizations.

Phase compositions of the as-synthesized specimens were characterized by Rigaku Ultima III X-ray diffractometer (XRD; Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation. Microstructure of the solidified CN-4 samples was observed using field-emission scanning electron microscopy (FESEM; Zeiss Ultra-55, Oberkochen, Germany). The chemical composition and elemental distribution were analyzed from the results of energy-dispersive X-ray spectrometer (EDX) attached with the FESEM equipment. Density of the densified CN-4 sample was measured from Archimedes method using water as the immersion medium. Vickers hardness was measured using a Vickers hardness tester (HV-1000 A) under a load of 49 N with 15 s holding duration. At least 7 measurements were conducted to get the average values of density and Vickers hardness.

3. Thermodynamic calculation of designed SHS reactions

Thermodynamic reactivity is an important factor to predict whether the SHS combustion can be ignited and sustained. Merzhavov has proposed that a combustion reaction could be sustained when the adiabatic temperatures (T_{ad}) was higher than 1800 K [54]. Thus, the SHS reactant composition can be designed and adjusted from the T_{ad} calculations [55]. In this study, T_{ad} values of the SHS reaction systems with different oxidants and TiO_2/Ti ratios were investigated. The T_{ad} parameter of a chemical reaction can be computed using the following equations [45,56]:

$$\Delta H^0_{298} + \sum_{n_i}\left(H^0_T - H^0_{298}\right)_{i.product} = 0 \tag{1}$$

$$\Delta H^0_{298} = \int_{298}^{T_{tr}} C_p dT + \Delta H_{tr} + \int_{T_{tr}}^{T_m} C_p' dT + \Delta H_m + \int_{T_m}^{T_B} C_p'' dT + \Delta H_B + \int_{T_B}^{T_{ad}} C_p''' dT \tag{2}$$